The marriage of ferrocene and silicotungstate: An ingenious heterogeneous Fenton-like synergistic photocatalyst

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ABSTRACT

The oxidation of 4-chlorophenol (4-CP) was firstly carried out by heterogeneous Fenton-like process in the presence of ferrocene-containing silicotungstate catalyst (denoted as FcSiW). The catalyst was successfully prepared by precipitation method in aqueous solution using ferrocene (Fc, or CpFeCp) and silicotungstic acid (SiW, or $H_4SiW_{12}O_{40}\cdot xH_2O$) as raw materials and the intrinsic relationship between structure and catalytic activity was fully studied. Under the suitable conditions, the prepared FcSiW exhibited high catalytic activity, especially under irradiation conditions. Moreover, the catalyst showed good reusability without significant performance drop after successive experimental runs and high stability with very low iron leaching. The strong interaction resulting from the close contact between Fc and polyoxometalate (POM) species contributes to the charge-transition from Fc to POM, which is in favor of its photocatalysis. A possible catalytic mechanism revealing the synergistic effect between the Fenton-like reaction of ferricinium and photocatalysis of $SiW_{12}O_{40}^{4-}$ anions in FcSiW/H_2O_2 system was proposed on the basis of experiment results and previous reports. This novel highly active heterogeneous catalyst has the potential for wide range of application in wastewater pollutants treatment.

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1. Introduction

Homogeneous Fenton oxidation process in Fe^{2+}/H_2O_2 system has proven to be efficient and powerful for degradation of various organic pollutants in water, in which most of organics can be mineralized to CO_2, H_2O, and other inorganic matters [1,2]. However, this approach suffers from many drawbacks, such as being efficient only at acidic pH values (usually pH 3), addition of high concentration of ferrous salt, and requiring post-treatment of iron ions and massive sludge of iron hydroxide. Heterogeneous Fenton-like processes using solid materials as the catalysts are the alternatives, in which the catalysts can be facilely recovered and recycled, and the post-treatment of iron ions in water and sludge is avoided [3]. Many iron-containing materials such as zero valent iron (ZVI), iron oxides

or related materials, ferrimolybdate, bismuth ferrite, pyrite [4,5], et al. have been studied as heterogeneous Fenton-like catalysts.

Ferrocene (Fc) is a prototypical metallocene, which is insoluble and highly stable in water. It consists of two cyclopentadienyl anions bound on opposite sides of a central ferrous ion [6]. The electron donor-acceptor conjugated structure of Fc makes it a potential heterogeneous Fenton-like catalyst. However, there are few reports on the applications of ferrocene and related materials in heterogeneous Fenton-like processes. Previous literatures have investigated the wastewater treatment employing heterogeneous Fenton-like system by immobilizing Fc on mesoporous molecular sieve SBA-15 [7], mesostructured silicates MCM-41[8], single-wall carbon nanotube (SWCNT) [9]. Hu et al. [10] has reported that SiO_2-C_2H_4-ferrocene with covalent grafting of ferrocene on functionalized silica with a $-C_2H_4-$ linkage exhibited high photocatalytic activity in the degradation of Acid Red B under UVA ($\lambda_{max} = 365$ nm), especially in the presence of H_2O_2. Recently, Tian et al. [11,12] demonstrated the catalysis of pure ferrocene for degradation of methylene blue in heterogeneous ferrocene/H_2O_2 system, and ver-

ified the optimal condition of pH 3 and poor performance at pH higher than 5. Rationally, ferrocene-related materials are the alternative catalysts for heterogeneous Fenton-like processes.

Polyoxometalates (POMs) are a group of multi-metal oxygen clusters with the ability to undergo multi-electron transfer reversibly [13,14]. These compounds have been intensively studied as one kind of new photocatalysts. Upon irradiation with light energy higher or equal to the HOMO–LUMO gap of POMs, electron-transfer from O^{2-} to M^{6+} (M = W, Mo) occurs at Mo—O—Mo bonds, resulting in the formation of excited POMs (POMs*) with strong oxidation power to directly oxidize organic pollutants [15,16]. The reduced POM (POMs$^-$) can be re-oxidized by O_2 dissolved in water to accomplish the catalytic redox cycle. Moreover, some authors suggested that organics can be simultaneously oxidized by HO$^•$ produced from the activation of H_2O by POM*. The excited POMs* has a strong ability to hold and accumulate electron during the photoreductive process and make POMs very different from other semiconductor, such as TiO_2, where the photo-induced electron accumulation is negligible during reaction [17]. Recently, the applications of POMs in Fenton or related processes have caused great attentions. For example, Choi et al. [18] reported that $SiW_{12}O_{40}^{4-}$ or $PW_{12}O_{40}^{3-}$ in Fe°/O_2 system could mediate the electron transfer from Fe° to O_2 to produce Fenton reagent, Fe^{2+} and H_2O_2. Sedlak et al. [19] demonstrated that addition of $PW_{12}O_{40}^{3-}$ in Fe^{3+}/H_2O_2 homogeneous system could extend the working pH range up to pH 8.5. Our group has also found that some water-insoluble complexes containing both iron and heteropolyanion have high catalytic activity for heterogeneous Fenton-like oxidation processes [20,21]. All these studies in the literature implied the potential synergies between iron and POM for the catalytic oxidation of pollutants by H_2O_2.

It has been reported the indirect conjugation of ferrocene with POMs through a Mo—N imido bond [22] or through an extend π-conjugated bridge [23]. These kinds of charge-transfer hybrids with ferrocenyl units covalently attached to a heteropolyanion cluster showed a clear charge transition from the ferrocenyl donor to the cluster acceptor over these hybrids. Considering the intrinsic Fenton-like catalytic property of ferrocene and the possible promotion of POMs in the oxidation of organics, it is reasonable to infer that the water-insoluble complexes of ferrocene with POMs may be a kind of active heterogeneous Fenton-like catalysts. In this paper, a complex (FcSiW) between ferrocene (Fc) and silicotungstic acid (SiW) was firstly synthesized and its catalytic performance for the degradation of 4-chlorophenol (4-CP) was studied in heterogeneous FcSiW/H_2O_2 system. A possible reaction mechanism was also proposed.

2. Experimental

2.1. Reagents

Ferrocene was purchased from ShengAo Chemical Reagent Co., Ltd. Silicotungstic acid and hydrogen peroxide (30 wt.%) were obtained from Sinopharm Chemical Reagent Beijing Co., Ltd. 4-CP was provided by Tianjin Guangfu Fine Chemical Industry Research Institute. All the reagents were analytical grade and used without further purification. Deionized water was used throughout the investigation. The solution pH was adjusted by a diluted aqueous solution of dilute H_2SO_4 or NaOH.

2.2. Preparation and characterization of FcSiW

For synthesis of FcSiW catalyst, 0.5 g of ferrocene was firstly dissolved into 10 mL of concentrated sulfuric acid, resulting in a deep red solution with strong blue fluorescence. This phenomenon is the

consequence of formation of ferricinium cation from the oxidation of ferrocene [24]. After 1 h of stirring, the solution was diluted with 150 mL of deionized water, and then a silicotungstic acid solution (20 mL, 0.043 mol L^{-1}) was added dropwise, producing FcSiW azure precipitate. After being stirred at ambient temperature for 3 h, the deep blue FcSiW powder was obtained by collecting the precipitate by centrifuging, washing with deionized water, and drying at 60 °C.

Fourier transform infrared spectrometer (FT-IR, Shimadzu IRAffinity-1, KBr pellet), thermogravimetry (TG, SeikoTG/DTA 6300), UV–vis diffuse reflection spectrometer (UV–vis DRS, Shimadzu UV-2550, BaSO$_4$ reference) were used to characterize the resulted FcSiW, ferrocene, and silicotungstic acid samples, respectively. The composition of prepared FcSiW was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, Shimadzu ICPS-7510). The micromorphology of the materials was determined by a JEOL 6301F scanning electron microscope (SEM). Additional information was gathered with an energy-dispersive X-ray spectroscopy (EDS) detector. X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Analytical AXIS 165. All the spectra were referenced to a C$_{1s}$ binding energy of 284.8 eV, and were fitted using Gaussian–Lorentzian peak shapes and Shirley baselines.

2.3. Catalytic degradation of 4-CP

Degradation of 4-CP was conducted in FcSiW/H_2O_2 system under both the dark and irradiated conditions. All experiments were carried out in a jacketed cylindrical quartz tube, and the reaction temperature was controlled (± 0.2 °C) with a thermostatic bath. A 250 W high pressure mercury lamp with a maximum emission at about 365 nm was used as the source of irradiation, which was surrounded by a quartz jacket to allow for water-cooling. The light flux at the liquid level was tested to be ca. 90 μW cm^{-2}.

In a typical procedure, a certain amount of FcSiW powder was added into 100 mL of 4-CP solution, and the suspension was stirred in the dark for 30 min to reach the adsorption-desorption equilibrium of 4-CP on surface of the catalyst. Then the pH of the suspension was adjusted using dilute H_2SO_4 or NaOH solution, followed by the addition of H_2O_2. No pH control was performed throughout the whole process. For photo-assisted Fenton-like process, the reaction system was simultaneously upon irradiation with the addition of H_2O_2. Specimens were withdrawn at regular time intervals and analyzed immediately after filtration through a 0.22 μm filter to remove the FcSiW powder. Experiments were carried out in triplicate, and all the results were expressed as a mean value.

2.4. Analytical methods

The concentration of 4-CP was determined by using a high performance liquid chromatograph (HPLC, Shimadzu LC-20AD) equipped with a C18 reverse phase column (250 × 3.0 mm) and an UV detector. The mobile phase was a mixture of methanol (65%) and 1% of acetic acid aqueous solution (35%) at the flow rate of 0.5 mL min^{-1}. Total organic carbon (TOC) was obtained by a TOC analyzer (Shimadzu TOC-V CPH).

3. Results

3.1. Characterization of FcSiW

The composition of prepared FcSiW is proposed to be [Fe(C$_5$H$_5$)$_2$]$_3$(H$_3$O)SiW$_{12}$O$_{40}$ according to the ICP-AES and TG data. Anal. Calcd. for FcSiW (wt%): Fe, 4.85; Si, 0.81; W, 63.9. Found by ICP-AES (wt%): Fe, 4.90; Si, 0.78; W, 64.5.
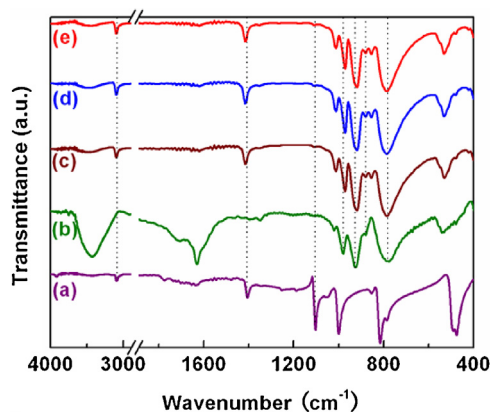
Fig. 1. FT-IR spectra of (a) ferrocene; (b) silicotungstic acid; (c) fresh FcSiW catalyst; (d) the FcSiW catalyst used in the dark; (e) the FcSiW catalyst used under irradiation.

FT-IR spectra of silicotungstic acid, ferrocene and the various FcSiW are presented in Fig. 1. Ferrocene shows the characteristic absorption bands at 3094 cm^{-1} (νC—H), 1406, 1105 cm^{-1} (νC=C), 1000 cm^{-1} (βC—H), 816 cm^{-1} (γC—H) and 474 cm^{-1} (ν_{as}Feπ_6, $\gamma_{as}\pi_6\pi_6$) [25]. Silicotungstic acid displays the IR fingerprint of Keg-

gin structured cluster at 980 cm^{-1} (ν_{as}W=O), 926 cm^{-1} (ν_{as}Si–O), 877 cm^{-1} (ν_{as}W–O$_b$–W) and 775 cm^{-1} (ν_{as}W–O$_c$–W) [9].

Compared with silicotungstic acid, FcSiW exhibits the similar IR feature in the region of 1000–700 cm^{-1}. The absorptions at 972 cm^{-1} (ν_{as}W=O), 920 cm^{-1} (ν_{as}Si–O), 881 cm^{-1} (ν_{as}W–O$_b$–W) and 787 cm^{-1} (ν_{as}W–O$_c$–W) indicate the retainment of Keggin structure in the prepared FcSiW. Additionally, we can also identify the structural information about ferrocinium in the IR spectrum of FcSiW at the wavenumbers greater than 1000 cm^{-1}. The absorption bands at 3099 cm^{-1} (νC—H), 1416 and 1110 cm^{-1} (significantly weakened νC=C) implies the existence of ferrocinium cation in FcSiW. The absorptions of ferrocinium below 1000 cm^{-1} can not be discriminated, possibly being overlapped with those in this region from Keggin structured SiW$_{12}$O$_{40}$$^{4-}$ heteropolyanion. The changes in strength and position of the absorption bands may be due to the interaction between SiW$_{12}$O$_{40}$$^{4-}$ heteropolyanion and ferrocinium.

TG curves of silicotungstic acid, ferrocene and FcSiW are presented in Fig. 2. For silicotungstic acid, the 4.2% weight loss from ca. 45–250 °C is due to the loss of crystallization water, and 1.1% weight loss from ca. 300–550 °C is ascribed to destruction of Keggin structure to SiO$_2$ and WO$_3$. Therefore, the composition of the silicotungstic acid used in this study is determined to be H$_4$SiW$_{12}$O$_{40}$·7H$_2$O, with theoretical weight loss values of 4.2% and 1.2%, respectively. The TG result showes no obvious change in TG
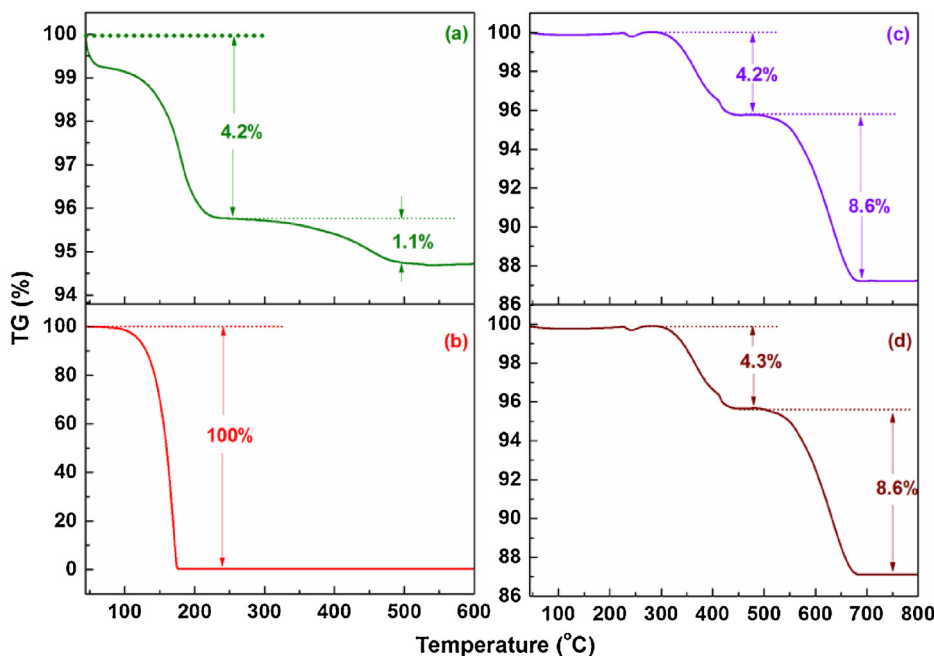

Fig. 2. TG curves of (a) silicotungstic acid, (b) ferrocene, (c) the prepared FcSiW and (d) used FcSiW.
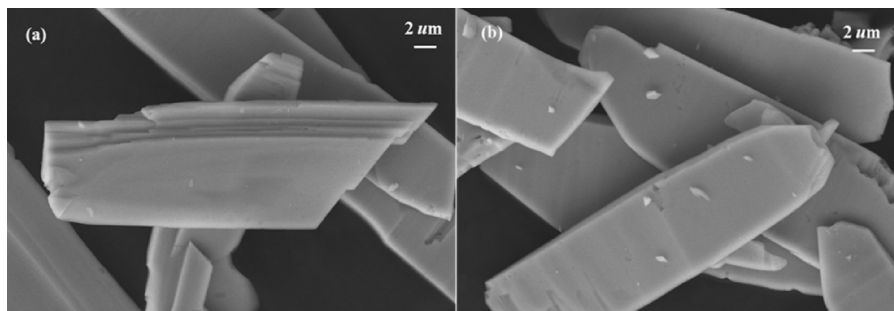

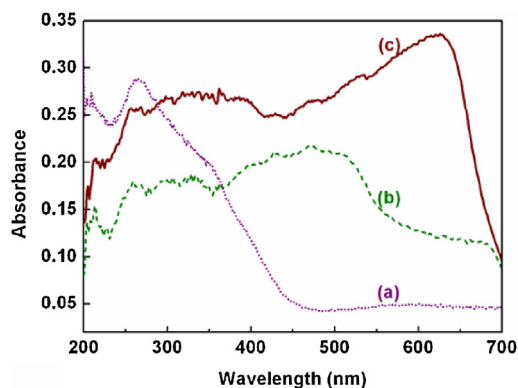**Fig. 3.** SEM images of (a) fresh and (b) used FcSiW samples.

Fig. 4. UV–vis DRS of (a) silicotungstic acid, (b) ferrocene and (c) FcSiW.

behavior for the used FcSiW samples, indicating no changes of chemical composition after photocatalytic reactions.

It is known that ferrocene sublimates at ca. 100 °C, and decomposes to metallic iron, hydrogen, and various hydrocarbons at ca. 400 °C[8]. Thus, as shown in Fig. 2b, the gaseous ferrocene generated by sublimation is transported out of furnace by nitrogen flow in TG measurement, resulting in almost 100% weight loss in the range of ca. 100–174 °C. However, the TG curve of FcSiW (Fig. 2c) indicates that the weight loss occurs only when the temperature is raised above 300 °C, and the weight loss of FcSiW at such high temperature is unlikely due to the sublimation of ferrociniuim cation, possibly related to its decomposition. Therefore, the 4.2% weight loss from ca. 300–450 °C is possibly due to decomposition of one of the three ferrocinium cations and the loss of crystallization water simultaneously (calcd 4.3%). The 8.6% weight loss from ca. 500–690 °C is resulted from decomposition of the remaining two ferrocinium cations and destruction of the Keggin structured heteropolyanion, with residue of Fe, SiO_2 and WO_3 (calcd 8.5%). The observation that one of the three ferrocinum cations decomposes at a relative lower temperature is possibly due to its different way of bonding in FcSiW. The structure of the prepared FcSiW awaits further study.

Fig. 3 show the SEM images of fresh and used FcSiW samples after Fenton oxidation test. Both the fresh and used catalysts exhibit the tabular cuboid shape with a very smooth surface. The average width is around $20 \sim 30\,\mu m$ with length up to $100\,\mu m$. It is also clear that the running of Fenton process did not change significantly on its structure.

The UV–vis DRS of silicotungstic acid, ferrocene and FcSiW are shown in Fig. 4. Silicotungstic acid displays an absorption band in the range of ca. 200–450 nm with the peaks at 210 and 265 nm, corresponding to the charge transfer from O^{2-} to W^{6+} at W = O and W—O—W bonds, respectively[17]. A weak wide absorption peak ranged from 500 to 650 nm is due to d–d transition typical for octahedral M^{2+} with six oxygen bond ligands [26]. The band at around 215 nm is assigned to charge-transfer the obrital located on the Cp ring, and the position is the same as those reported for the ferrocene in sulution [27]. The absorption bands of ferrocene around 330 and 470 nm are assigned to ligand field bands from the splitting of the d levels of Fe^{2+}. However, as for the FcSiW sample, its absorption band is different form that of the starting POM or the ferrocene, whereas a broad absorption band peaked at ca. 620 nm appears with redshift absorption and the absorption threshold onset that continuously extended from ultraviolet to the visible region [26]. This new absorption in the visible region corresponding to relatively low band gap energy can be ascribed to charge-transfer transitions between the ferrocinium cation and heteropolyanion. The broad absorption range of FcSiW is possibly in favor of its photocatalysis.

3.2. Catalytic performance of FcSiW

3.2.1. Overall comparison

The catalytic performance of FcSiW was evaluated by catalytic oxidation of 4-CP in the presence of H_2O_2, under the conditions of 4-CP 50 mg/L, H_2O_2 10 mM, FcSiW 0.1 g/L, temperature 35 °C and initial pH 6.5. All the experiments were carried out in the dark and under irradiation separately. Control experiments with addition of the catalyst alone or H_2O_2 alone indicated that no evident 4-CP degradation occurred within the observed time. However, as shown in Fig. 5, when both the FcSiW and H_2O_2 were added, 4-CP was degraded remarkably. In addition, as showed in Fig. 5a and b, pure ferrocene shows no activity for oxidation of 4-CP, while the oxidation activity for FcSiW is much higher than the starting POM or ferrocene parents, both under irradiation and in the dark.

The complete disappearance of 4-CP was accomplished in ca. 100 min under irradiation and ca. 110 min in the dark, separately. With respect to the decrease in 4-CP concentration in the reaction system, it seems that the effect of irradiation is not significant. However, TOC measurement indicated that the mineralization of 4-CP was considerably promoted when the reaction was conducted under irradiation. After 6 h of reaction, the 89.5% TOC removal was achieved under irradiation, and in contrast, only 20.5% was obtained in the dark.

3.2.2. Effect of H_2O_2 concentration

To investigate the effect of H_2O_2 concentration on Fenton-like degradation of 4-CP, different H_2O_2 concentrations of 5, 8, 10 and 12 mM were performed under irradiation and in the dark, respectively. The initial reaction conditions are as follows: catalyst dose of $0.1\,g\,L^{-1}$, initial 4-CP concentration of $50\,mg\,L^{-1}$, pH 6.5 and temperature of 35 °C. As shown in Fig. 6, the degradation of 4-CP is enhanced with increasing H_2O_2 concentration from 5 to 10 mM. The result may be attributed to more hydroxyl radicals (HO•) generating with increasing the amount of H_2O_2. However, when the H_2O_2 concentration is increased to 12 mM, the degradation efficiency of 4-CP is slowed down. This result indicated that higher concentration of H_2O_2 inhibited the degradation of 4-CP, which can be due to the scavenging reaction of hydroxyl radicals between H_2O_2 and HO•[28,29].

3.2.3. Effect of catalyst dose

The effect of catalyst dose on Fenton-like degradation of 4-CP was examined at different amounts of catalyst ranging from $0.05\,g\,L^{-1}$ to $0.3\,g\,L^{-1}$ under irradiation and in the dark, respectively. The initial reaction conditions are as follows: H_2O_2 concentration of 10 mM, initial 4-CP concentration of $50\,mg\,L^{-1}$, pH 6.5 and temperature of 35 °C. Fig. 7 illustrates that the degradation efficiency of 4-CP increases with increasing the catalyst dose. The result could be due to the increasing number of active sites on the catalyst surfaces which were favorable to the degradation of 4-CP.

3.2.4. Effect of solution pH

The effect of solution pH on Fenton-like degradation of 4-CP was performed at different pH values ranging from 2 to 9 under irradiation and in the dark, respectively. Other initial reaction conditions were fixed at H_2O_2 concentration of 10 mM, catalyst dose of $0.1\,g\,L^{-1}$, initial 4-CP concentration of $50\,mg\,L^{-1}$ and temperature of 35 °C. As shown in Fig. 8, with decreasing the solution pH from 6.5 to 3, the degradation of 4-CP is remarkably enhanced. It implied that the degradation efficiency of 4-CP was apparently improved at strong acidic pH value (pH = 3). Nevertheless, the degradation of 4-CP was largely halted as the pH value decreased to 2 rather than enhanced, which was more marked when the reaction performed in the dark. At lower pH value (pH = 2), the suppression of 4-CP degradation may be due to the higher stability of the oxidant at acidic
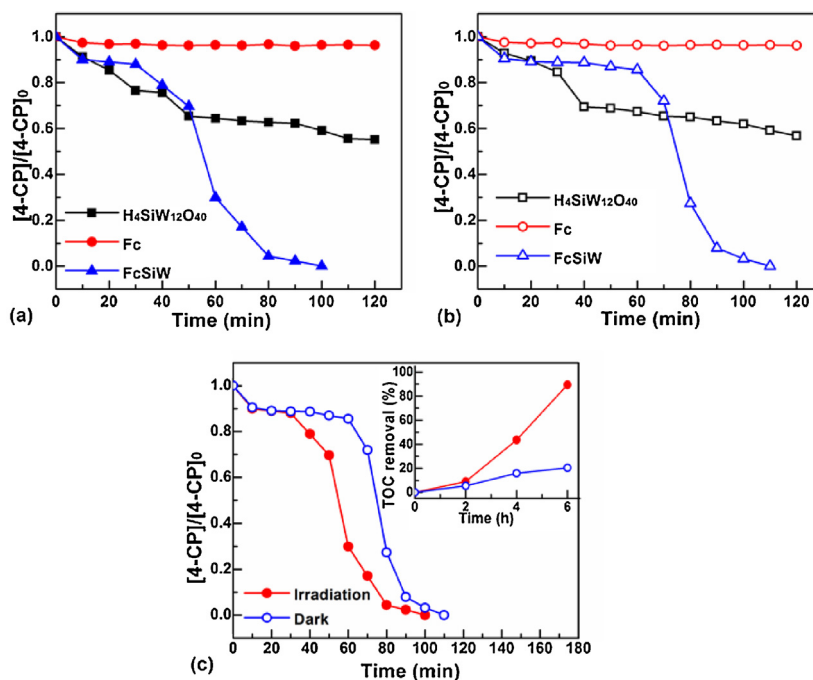
Fig. 5. Degradation of 4-CP: (a) under irradiation and (b) in the dark over various catalysts; (c) the performance comparison over FcSiW catalyst under irradiation and in the dark. The insert in (c) shows TOC removal.
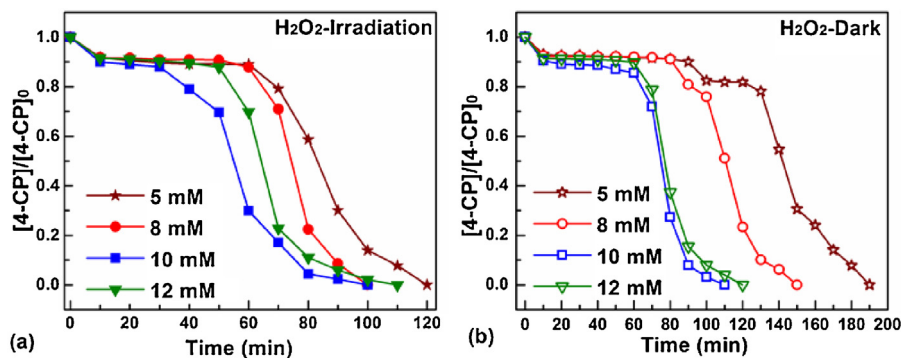

Fig. 6. Effect of H_2O_2 concentration on Fenton-like degradation of 4-CP: (a) under irradiation; (b) in the dark.
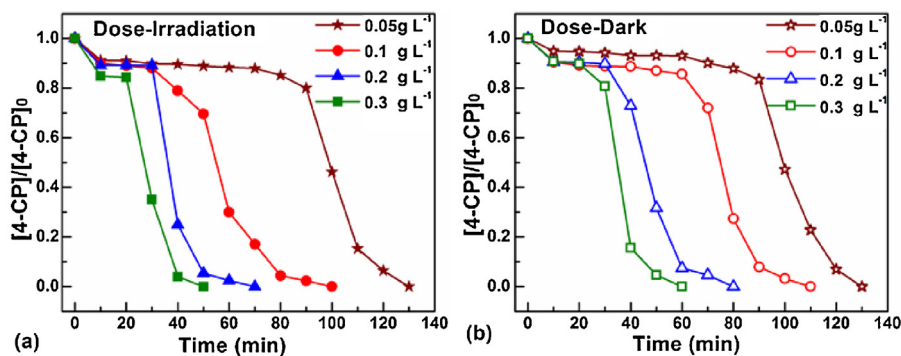

Fig. 7. Effect of catalyst dose on Fenton-like degradation of 4-CP: (a) under irradiation; (b) in the dark.

pH values that decreases the formation of radicals [30]. Moreover, in alkaline conditions (pH = 8, 9), there is little degradation of 4-CP both in the dark and under irradiation. This is probably connected with lower stability of the oxidant at alkaline pH values that favors the decomposition of H_2O_2 into H_2O and O_2 instead of generation active species [31,32].

3.2.5. Effect of temperature

In order to clarify the effect of temperature on Fenton-like degradation of 4-CP, a series of experiments were carried out with a temperature range of $25 \sim 40\,^{\circ}$C at H_2O_2 concentration of 10 mM, catalyst dose of $0.1\,g\,L^{-1}$, initial 4-CP concentration of $50\,mg\,L^{-1}$ and pH 6.5, respectively, and results are illustrated in Fig. 9. It can
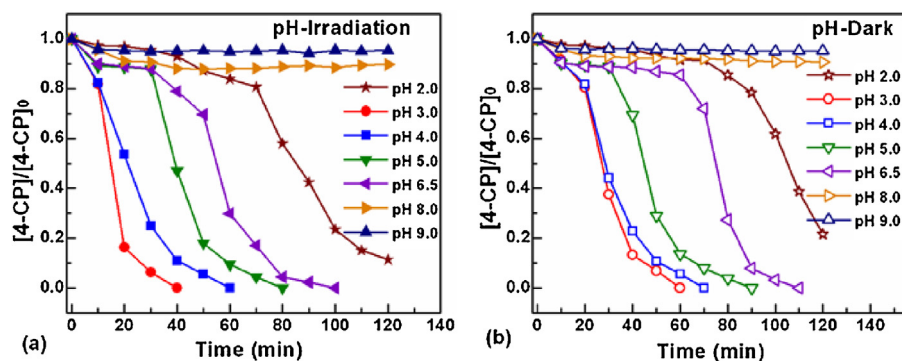
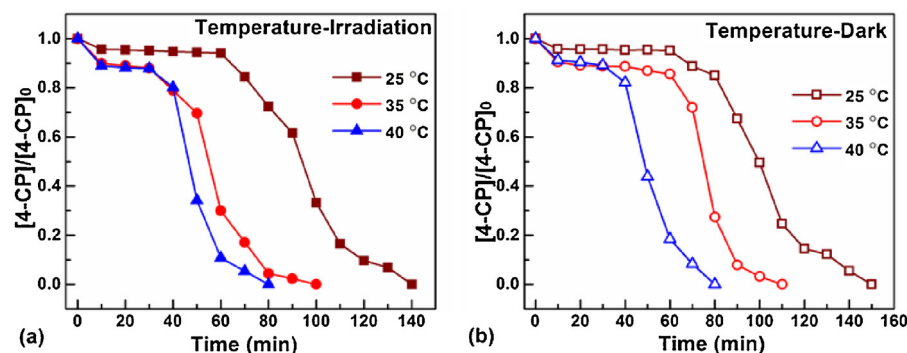**Fig. 8.** Effect of solution pH on Fenton-like degradation of 4-CP: (a) under irradiation; (b) in the dark.

Fig. 9. Effect of temperature on Fenton-like degradation of 4-CP: (a) under irradiation; (b) in the dark.
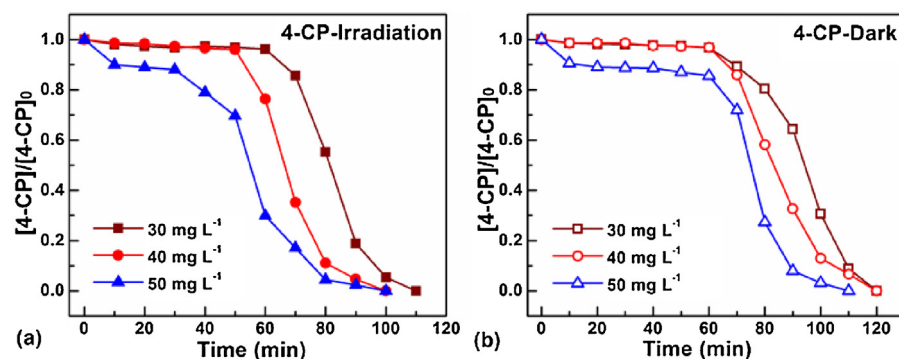

Fig. 10. Effect of initial concentration of 4-CP on Fenton-like degradation of 4-CP: (a) under irradiation; (b) in the dark.

be seen that higher temperature improves the degradation of 4-CP in the range of $25 \sim 40\,^{\circ}\text{C}$, which is consistent with Arrhenius law. The temperature accelerating Fenton-like degradation of 4-CP may be explained by the enhancement of generation rate of hydroxyl radicals [33–35]. However, under irradiation, the degradation rate of 4-CP did not show a significant difference with the increase in temperature from 35 to $40\,^{\circ}\text{C}$ (95.6% at $35\,^{\circ}\text{C}$ and 100% at $40\,^{\circ}\text{C}$) after 80 min of reaction. Moreover, hydrogen peroxide tends to decompose into H_2O and O_2 at higher temperature, which is bad for the degradation of 4-CP. Therefore, temperature of $35\,^{\circ}\text{C}$ was selected as the optimum reaction condition.

3.2.6. Effect of initial concentration of 4-CP

Several experiments were performed to study the effect of different initial concentration of 4-CP (30, 40 and $50\,\text{mg}\,\text{L}^{-1}$, respectively) on Fenton-like degradation of 4-CP with fixing H_2O_2 concentration, catalyst dose, temperature and pH value at 10 mM, $0.1\,\text{g}\,\text{L}^{-1}$, $35\,^{\circ}\text{C}$ and 6.5, respectively. As shown in Fig. 10, the degra-

dation of 4-CP is clearly improved both under irradiation and in the dark when the initial concentration of 4-CP is increased from 30 to $50\,\text{mg}\,\text{L}^{-1}$. This result may be ascribed to that the higher concentration of 4-CP is advantageous to the full occupation of adsorption sites on the catalyst surface [36]. As a result, the active sites on the catalyst surface are fully employed, which improves the degradation efficiency of 4-CP. Furthermore, the phenomenon may also be ascribed to the excessive dosage of H_2O_2 for low initial concentration (30 and $40\,\text{mg}\,\text{L}^{-1}$) of 4-CP resulting in the scavenging of hydroxyl radicals.

3.2.7. Reusability and stability

For the heterogeneous catalyst, it is important to evaluate the reusability and stability of catalyst for the purpose of industrial implements. As shown in Fig. 11, the reusability of FcSiW was evaluated with reaction conditions of catalyst $0.1\,\text{g}\,\text{L}^{-1}$, H_2O_2 10 mM, 4-CP $50\,\text{mg}\,\text{L}^{-1}$, pH 6.5 and T $35\,^{\circ}\text{C}$. The catalytic behavior of FcSiW was tested during three consecutive experimental runs under
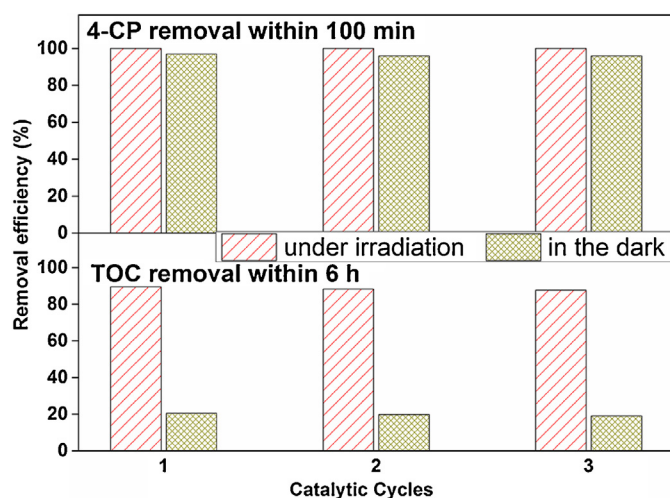
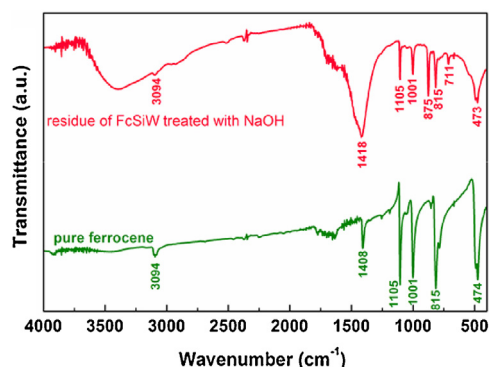**Fig. 11.** Reusability of FcSiW for 4-CP degradation.

Fig. 12. FT-IR spectra of pure ferrocene and residue of FcSiW after treatment with sodium hydroxide.

irradiation and in the dark. After 100 min of reaction, 4-CP was completely degraded with fresh and reused catalysts under irradiation; 4-CP removal efficiencies in the dark were 97%, 96%, 96%, respectively. After 6 h of reaction, TOC removal efficiencies under irradiation were 89.5%, 88.3%, 87.6%, while those were 20.5%, 19.8%, 19.1% in the dark, respectively. The iron leaching was determined by ICP-AES. The FcSiW exhibited good stability since the iron leaching was no more than European Union standard for the catalyst.

4. Discussions

The catalytic performances reported above show the development of a novel stable organic-inorganic hybrid with the inclusion of ferrocene and POMs. This ingenious complex show high photoactive Fenton catalytic activity towards degradation of organic water pollutants, such as 4-CP, with high TOC removal efficiency. In addition, the consecutive test results exhibit that these catalysts have good reusability during Fenton process with low iron leaching. The intrinsic relationship between structure and activity for this novel FcSiW complex can be the reason for the good catalytic activity for 4-CP oxidation.

FT-IR spectra of pure ferrocene and the residue samples of FcSiW after treatment with sodium hydroixde are presented in Fig. 12. After the removal of silicotungstic acid by treating with NaOH, the remainder is ferrocene, as indicating by the FT-IR characterization that the IR spectra for the residue shows the characteristic adsorption bands the same with that for ferrocene. The characteristic absorption bands at 3094 cm^{-1} (νC—H), 1406, 1105 cm^{-1} (νC═C),

1000 cm^{-1} (βC—H), 816 cm^{-1} (γC—H) and 474 cm^{-1} (ν_{as}Feπ_6, $\gamma_{as}\pi_6\pi_6$) are all reserved for the treated samples [25]. This result indicates that the ferrocene was not damaged during the complex fabrication process, even on concentrated sulfuric acid solution.

In addition, surface characterization by nanoscale elemental STEM-EDX mapping was used to determine the surface distributions of Fe, Si and W species on the FeSiW catalysts. The distribution domains of the Fe, Si and W species clearly overlap each other on both fresh and used catalysts (Fig. 13b–e and g–j), demonstrating that via the solidification process, the Fe species in Fc are highly dispersed into the SiW texture and are in close contact with the heteropolyanion. The Fenton process did not change the catalyst's appearance, as identified by the used sample's image in Fig. 13f since no significant changes between the fresh and used samples.

In the case of the ferrocene-polyoxotungstate composite, the diffuse reflectance (UV-vis) spectrum of the FcSiW composite in Fig. 4 showed a pronounced low-energy peak that extended to infrared region. Spectral (digital) subtraction of the component spectra yielded the difference spectrum (Fig. 14) consists a new strong and very broad absorption band peaked at ca. 620 nm. This featureless band is due to the charge transfer between ferrocene and polyoxometalate anion ($[SiW_{12}O_{40}]^{4-}$) resulting the formation of W^v and the complex with mixed valence. Actually, there are some works reported in investigating desirable strategies to prepare new charge-transfer (CT) salts composes of polyoxometalates and ferrocene or ferrocenyl cations. A charge transfer salt (CpFe$^+$Cp)$_3$[W^{5+}W$^{6+}_5$O$_{19}$] composed of Lindqvist hexatungstate anions and ferrocenyl cations was synthesized with mixed-valence for POM as a result of one electron reduction by organic donor [37].

In our cases, when the deep red solution of ferrocene was mixed with the tungstate solution to form solid deposits, the color of reaction mixture changed from azure to deep blue. This remarkable color change suggests that partial W^{6+} have been reduced to W^{5+} to form mixed-valence polyoxotungstate anions. Here ferrocene act as a reductive agent to reduce W^{6+} to W^{5+} since no reductive reagent other than ferrocene was used. In other words, there is a strong charge transfer between Fc and SiW, and the Keggin-type polyoxometalate anions act as electron accpetor in the oxidation of electron-rich aromatic ferrocene via an initial electron transfer, resulting the self-assembling of mixed-valence SiW polyoxoanions with CpFe$^+$Cp in solid forms and precipitating out from the solution.

To aid our understanding of the charge transfer processes between Fc and SiW, we performed XPS measurements and investigated the surface chemical state of Fe species. The high resolution XPS scan of the Fe 2p region (Fig. 15) for both fresh and used FcSiW samples showed two major spin-orbit components Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$ at around 709 and 722 eV, respectively. There are two Fe 2p$_{3/2}$ peaks described as a mixed valence of Fe^{2+}/Fe^{3+} in ferrocene species, and curve fitting of these Fe 2p$_{3/2}$ peak envelopes has been applied to separate Fe^{2+} and Fe^{3+} data sets. The XPS binding energy for the 2p orbital of Fe^{2+} in ferrocene is 709.0 eV relative to C 1s at 284.8 eV, while for Fe^{3+} the binding energy is about 711.0 eV [38].

The Fe^{2+} signal is due to the ferrocene moiety, while the Fe^{3+} contribution can be unambiguously assigned to the ferrocenium ion species, without signs of decomposition to iron oxide(s), such as Fe$_2$O$_3$, which is rely on the basis of the main peak-to-satellite Fe 2p$_{3/2}$ energy separation and of the relative intensity of Fe 2p$_{3/2}$ satellite to main lines in Fe$_2$O$_3$, as reported in previous study for surface-anchored ferrocenes [39,40]. This conclusion is also confirmed from the results showed in Fig. 12. The presence of ferrocenium is originated in the charge transfer process between Fc and SiW, and the overall +1 charge of the ferrocene species could be neutralized by heteropolyanion groups. The higher area of Fe^{2+} peak with a Fe^{2+}/Fe^{3+} ratio around 4 suggesting a major Fe^{2+} population [41], and the presence of Fe^{3+}-related species indicates there
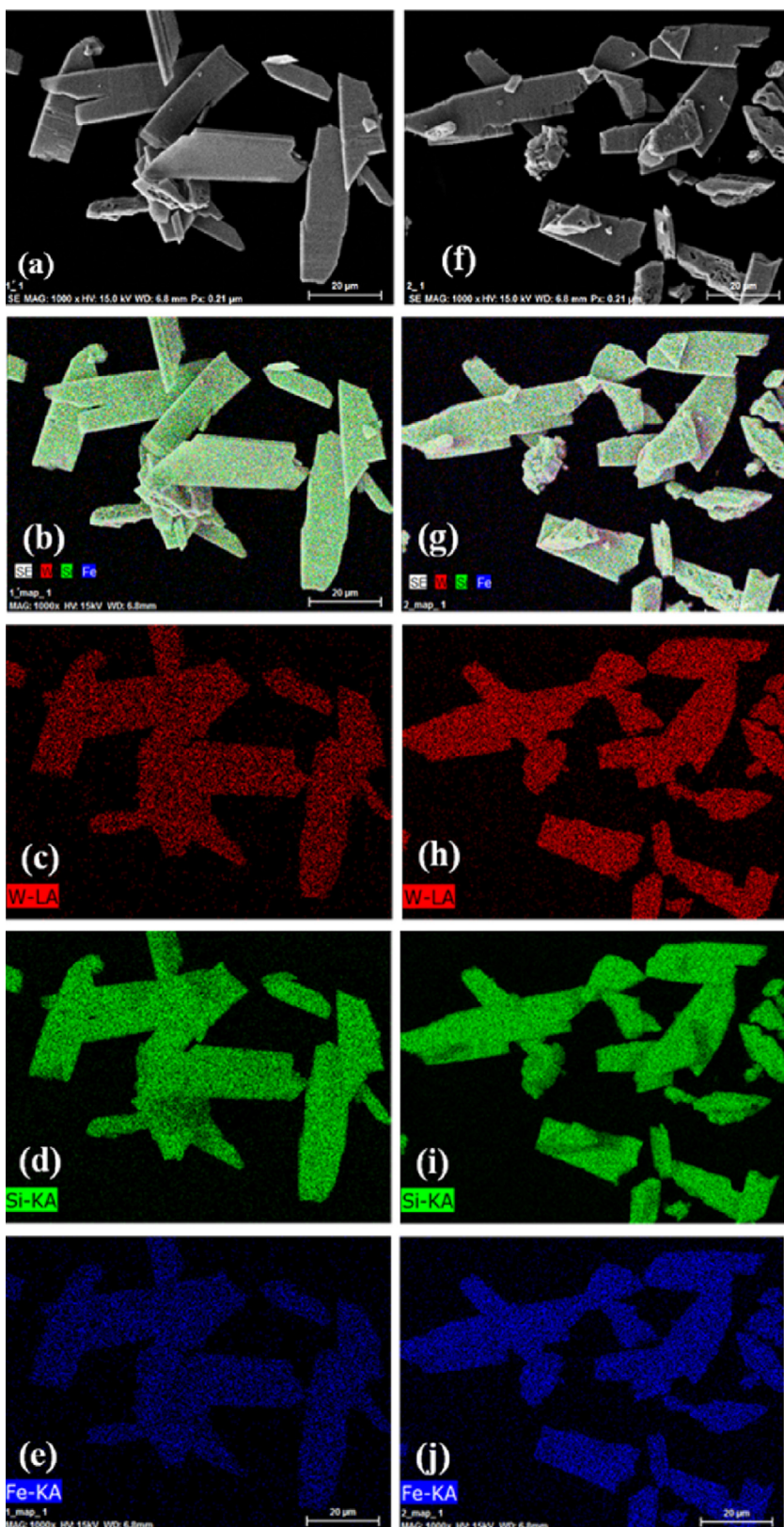
Fig. 13. SEM images for (a) fresh FcSiW and (f) used FcSiW after Fenton process; (b)–(e) Elemental EDX maps corresponded to the region in (a); (g)–(j) Elemental EDX maps corresponded to the region in (f). Both four maps represent the overlap intensity, measured W L intensity, Si K intensity and Fe K intensity, respectively.

was some extend of oxidation of the ferrocene units to ferricenium species after the inclusion of Fc and POM. The high proportion of Fe^{2+} could be beneicial for the high degradation effciency of organic pollutants. In addition, the broad ferricenium $2p_{3/2}$, or Fe^{3+} peak are much less precise and has been attributed to exchange interactions [42].

A Fc-SiW based approach to the formation of intramolecular charge transfer have been explored in this present investigation
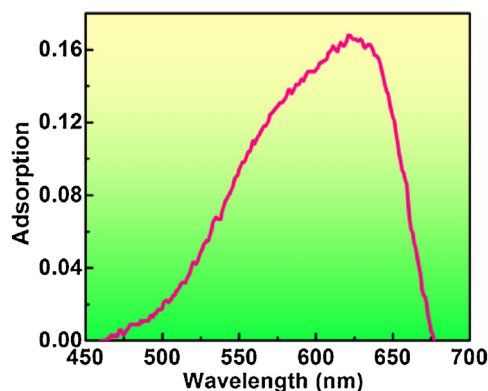
Fig. 14. Difference UV–vis DRS of FcSiW after subtracting the ferrocene and silicotungstic acid spectrum from the absorption spectrum of the FcSiW sample.
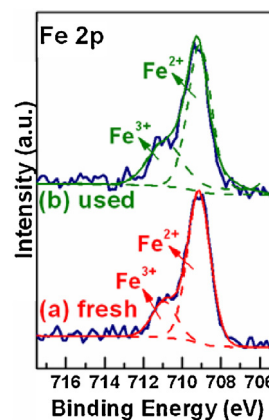

Fig. 15. XPS Fe 2p spectra for the fresh and used FcSiW samples.

with the partial irreversibility of Fe^{2+} oxidation, notably the robustness of the ferrocene/ferrocenium redox couple and its reversible circulation. In fact, an increasingly larger surface concentration of Fe^{3+} at the expenses of Fe^{2+} redox centers has been found from XPS analysis. After Fenton process, Fe^{2+} and Fe^{3+} components are still present, but the ratio of Fe^{2+}/Fe^{3+} has decreased to around 2.

One most-requested feature for the implement of heterogeneous Fenton catalyst on an industrial process is the stability with low leaching of iron species [3]. Therefore, effort aimed at the development of new catalysts which exhibit high stability with low deactivation and leaching will constitute a major factor. We found that the FcSiW exhibit quite high stability with low Fe species leaching duiring the Fenton process. This phenomenon can be explained by the special sturcture of FcSiW catalyst. The strong interaction resulting from the close contact between Fc and POM species contributes to the charge-transition from Fc to POM. The electrostatic binding of the corresponding ferrocenium group to the anionic polyoxometalate in the solid state represents the primary donor-acceptor attraction, as also showed in the interaction between $CpFeCpCH_2N^+(CH_3)_3$ and polyoxo-metalates [43]. The charge transfer character of the POM salts is enforced by the proximal tethering of the ferrocenyl group. Thus, the role of POM as an electron shuttle can be reinforced by this strong interaction.

The heterogeneous Fenton process with catalysts which display higher catalytic activity and stability is a promising technology in the field of wastewater treatment. Some catalysts exhibited the leaching of a significant amount of iron with pollutant degradation dominated by homogeneous Fenton reactions in the presence of leached iron species. However, in our work, the FcSiW-based heterogeneous catalysts display less leaching property. In these cases, Fenton reactions occurred on the surface of the catalyst.

In order to investigate the heterogeneous nature of the catalytic activity in $FcSiW/H_2O_2$ system, 0.01 g of catalyst was added into 100 mL of 4-CP (50 mg L^{-1}), after 60 min of stirring, the catalyst was removed from 4-CP solution. The result clearly indicated that no obvious 4-CP degradation was observed with subsequent addition of H_2O_2 into the above 4-CP solution after 2 h of stirring. Therefore, the heterogeneous Fenton-like degradation of 4-CP is likely to occur on or near the surfaces of the FcSiW, and the homogeneous Fenton reaction was nearly ignored.

To explore the mainly reactive oxidant generated in the $FcSiW/H_2O_2$ system, n-butanol, a well-known strong hydroxyl radial scavenger [28], was added into the mixture solution of FcSiW and 4-CP before H_2O_2 addition. The degradation of 4-CP was largely inhibited by n-butanol both under irradiation and in the dark systems within 120 min. Thus, hydroxyl radical may be the mainly reactive oxidant in the $FcSiW/H_2O_2$ system for the degradation of 4-CP.

The intermediates of degradation of 4-CP was monitored by HPLC from the solutions after degradation reaction. Some intermediates, such as hydroquinone, 1,4-benzoquinone, 4-chlorocatechol, pyrocatechol and 1,2,4-benzenetriol substances were detected both in dark and under irradiation conditions. There is almost no
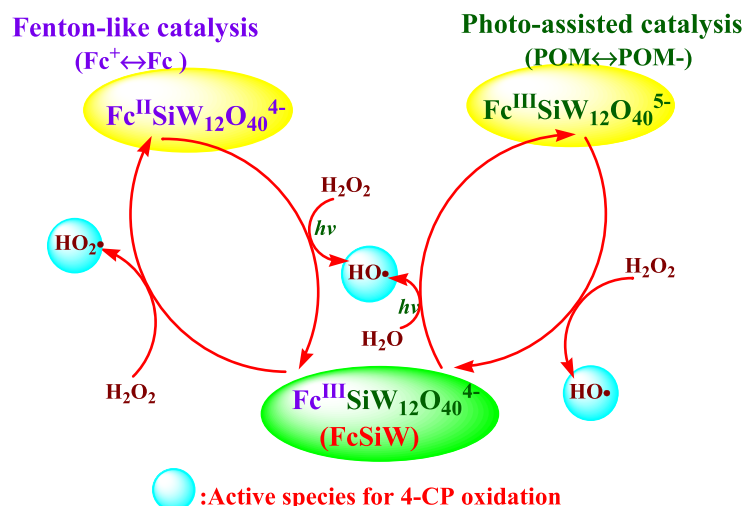

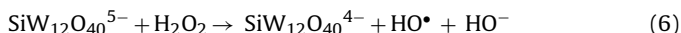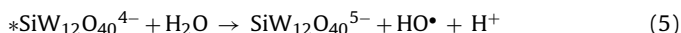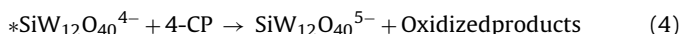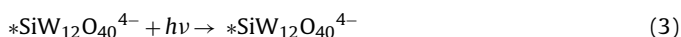**Fig. 16.** Possible catalytic mechanism of FcSiW for oxidation of 4-CP.

difference between the two conditions owing to the weak signals of these intermediate substances. The degradation of 4-CP was very slow at an initial phase, which may be due to the cyclic reaction between hydroquinone and 1,4-benzoquinone, resulting in the competitive oxidation between the intermediates and 4-CP, which largely inhibits the degradation of 4-CP. The suppression is probably removed once most hydroquinone is consumed, then degradation of 4-CP occurs quickly.

As effective photocatalysts, POM can absorb in the near visible and UV region of light spectrum ($\lambda < 400$ nm) and generate strongly oxidizing exited state POM*. Organics can be oxidized by POM* directly through charge transfer or H-atom abstraction, or via the intermediacy of solvent derived radicals. Afterwards, the reduced POM (POM$^-$) are usually re-oxidized by an electron acceptor such as O_2 [44–46]. Recently, Taghdiri et al. [27] reported the addition of silicotungstic acid into Fe^{2+}/H_2O_2 system could improve the degradation of hexamine. The high degradation efficiency was due to not only the increased production of hydroxyl radicals but also direct oxidation of hexamine by silicotungstate. A similar mechanism was also preliminarily proposed in our previous work [21], a highly active iron-containing silicotungstate catalyst was synthesized and used for heterogeneous Fenton oxidation of 4-CP.

A possible reaction mechanism of FcSiW was proposed based on the previous reports and the experimental results (Fig. 16). As mentioned above, ferrocene (Fc with Fe^{2+}) is easily oxidized to deep red ferricinium (Fc$^+$ with Fe^{3+}) when it dissolves in concentrated sulfuric acid. This is reversible reaction (Fc $\rightleftharpoons$ Fc$^+$). It was also reported that ferrocene could absorb ultraviolet light strongly [10,47,48]. Therefore, the hydroxyl radical was produced via the Fenton-like redox cycle Fc$^+$ $\rightleftharpoons$ Fc (Eqs. (1) and (2)) [10].

$$Fc^+ + H_2O_2 \rightarrow Fc + H^+ + HO_2^\bullet \tag{1}$$

$$Fc + H_2O_2 + h\nu \rightarrow Fc^+ + HO^- + HO^\bullet \tag{2}$$

This may be an explanation for the relatively slow degradation of 4-CP in the dark. When the oxidation of 4-CP was carried out under irradiation, the formation of hydroxyl radical was enhanced through Eq. (2). Furthermore, 4-CP could be also oxidized by the excited $SiW_{12}O_{40}^{4-}$ ($^*SiW_{12}O_{40}^{4-}$) directly or hydroxyl radicals produced by the reaction between $^*SiW_{12}O_{40}^{4-}$ and H_2O (Eqs. (3)–(5)).

$$^*SiW_{12}O_{40}^{4-} + h\nu \rightarrow {}^*SiW_{12}O_{40}^{4-} \tag{3}$$

$$^*SiW_{12}O_{40}^{4-} + 4\text{-CP} \rightarrow SiW_{12}O_{40}^{5-} + \text{Oxidized products} \tag{4}$$

$$^*SiW_{12}O_{40}^{4-} + H_2O \rightarrow SiW_{12}O_{40}^{5-} + HO^\bullet + H^+ \tag{5}$$

$$SiW_{12}O_{40}^{5-} + H_2O_2 \rightarrow SiW_{12}O_{40}^{4-} + HO^\bullet + HO^- \tag{6}$$

While the formed $SiW_{12}O_{40}^{5-}$ re-oxidized by O_2 was fairly slow [46] and the recycling of $SiW_{12}O_{40}^{5-} \rightleftharpoons SiW_{12}O_{40}^{4-}$ was greatly inhibited. Therefore, the degradation rate of 4-CP was negligible in the absence of H_2O_2. However, $SiW_{12}O_{40}^{5-}$ can be re-oxidized by H_2O_2, the addition of H_2O_2 may accelerate the conversion of $SiW_{12}O_{40}^{5-}$ to $SiW_{12}O_{40}^{4-}$ (Eq. (6)), leading to further generation of hydroxyl radicals according to Eqs. (5) and (6).

In conclusion, the mechanism for heterogeneous Fenton-like oxidation of 4-CP may be ascribed to the synergistic effect between the Fenton-like reaction of ferricinium and photocatalysis of $SiW_{12}O_{40}^{4-}$ anions in FcSiW/H_2O_2 system.

5. Conclusion

The heterogeneous Fenton-like catalyst FcSiW was successfully prepared using the co-precipitation of ferrocene and silicotungstic acid. The catalyst kept ferrocene and Keggin-structured $SiW_{12}O_{40}^{4-}$ anion well before and after reaction under irradiation or in the dark. The oxidation of 4-CP has been studied in

FcSiW/H_2O_2 system. The catalyst exhibits a high catalytic performance both in acidic and circumneutral conditions, and also shows good reusability according to three successive experimental runs and high stability with very low iron leaching. The irradiation has a positive effect on the oxidation of 4-CP, especially benefits to increase the TOC remove efficiency. The synergistic effect between the Fenton-like reaction of ferricinium and photocatalysis of $SiW_{12}O_{40}^{4-}$ anions in FcSiW/H_2O_2 system maybe both lead to the remarkable catalytic performance in heterogeneous Fenton-like oxidation of 4-CP. According to the promising catalytic activity exhibited in this work, the FcSiW catalyst is expected to play a significant role in the oxidation of wastewater pollutants.

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